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LA-UR-89-2630

TITLE   Geologic Containment of Radioactive Waste

LA-UR--89-2630

DE89 016993

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SUBMITTED TO   Proceedings for the Conference on Technology-Based
Confidence Building: Energy and Technology
July 10-14, 1989, Santa Fe, NM

DISCLAIMER

Received 1989

1989

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GEOLOGIC CONTAINMENT OF RADIOACTIVE WASTE

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GEOLOGIC CONTAINMENT OF RADIOACTIVE WASTE

Introduction

Geologic containment for the disposal of radioactive waste has been chosen or is being considered by many nations. Geologic disposal provides the multiple barriers concept for containment of long lived radioactive fission products and actinides in the waste material. The multiple barriers concept can be divided into two subsystems, 1) the engineered barriers, and 2) the natural barriers.

The engineered barriers consist of the waste form as a very slow dissolving material; the canister containing the waste form, providing complete containment as long as the canister is not breached by corrosion or physical destruction; a buffer and/or backfill material emplaced between that canister and the natural surroundings, which provides for slow migration of escaping radionuclides; and the last engineered barriers being any seals used to seal likely pathways such as boreholes, shafts, tunnels, or fracture zones.

The natural subsystem provides the final barrier to the escape of radionuclides to the accessible environment. The natural system, under expected conditions, could induce transport of radionuclides by interactions with groundwater and also, in the case of the unsaturated zone of Yucca Mountain, Nevada, through transport of volatile radionuclides in the gas phase. The natural system acts as an effective barrier to radionuclide migration because chemical reactions retard the movement of chemical species in the groundwater. These reactions include the precipitation and co-precipitation of stable crystalline phases; the reactions between species in solution with the surfaces of minerals (i.e. ion exchange, adsorption, etc.); and the formation and destruction or filtration of colloids. A model calculation by de Marsily, et al[1] of five hypothetical hydrogeological settings demonstrated that even under the most favorable hydrological conditions, retardation by chemical reactions was most effective. Therefore, it is very important to understand both the chemical and physical processes involved in the migration of radionuclides.

The performance assessment of the repository system requires the modeling of physical and chemical processes, many of them coupled. It also requires predictions of how this engineered and natural system will behave over a very long time (10,000 to 1 million years). By the very nature of the complexity of the processes that need to be understood and the long time scales over which predictions will be made large uncertainties with respect to the outcomes are inevitable.

Research programs must seek to reduce uncertainties in these predictions by way of site characterization, research into understanding the physical and chemical processes acting within this system, and developing techniques of modeling the processes of radionuclides migration within the natural system.

In this paper we present results of our work and outline our thoughts on resolving the uncertainties associated with the nature of the solubilities and speciation of actinides, the formation of radiocolloids, the sorption behavior of fission products and actinides and the transport mechanisms of advection, diffusion, and dispersion for radionuclides under environmental conditions thought to exist at Yucca Mountain, Nevada.

Solubility

It is not practical to measure the solubilities of all radionuclides that may exist in nuclear waste under all conditions that may occur at the repository and surroundings. Therefore, the technical approach used is based on three criteria: (1) select radionuclides that are expected to be present in large quantities; (2) select radionuclides that have solubility limits; and (3) select conditions that will bound expected conditions at the repository and along flow paths to the far field.

The radionuclides selected for initial study are neptunium, plutonium, and americium. These elements are expected to be present in the largest quantities and they have the longest radioactive half-lives. Measurements are also planned for uranium, thorium, radium, zirconium, tin, and nickel[2]. Radionuclides which have high solubilities in near-neutral pH groundwaters, such as cesium and technetium were not selected. It is expected that the solubilities of cesium and technetium will not be determined by solubility limits, but rather by dissolution rates of the waste package and adsorptive interactions with geologic media.

The repository and far field conditions that could affect the solubilities of radionuclides under consideration include numerous factors: temperature, pH, Eh, radionuclide oxidation state, concentration of complexing ligands, ionic strength, radiation field, etc. We will measure directly the "apparent" solubilities of radionuclides in groundwater samples obtained at the Yucca Mountain site. Groundwater samples with compositions that bracket the range of expected conditions at Yucca Mountain[3] will be taken from two sources. Water from Well J-13 is expected to be representative of the unsaturated zone near the proposed emplacement horizon (pH of 7, moderately oxidizing Eh, and a total carbonate

ion concentration of $\sim 10-3$ $\underline{M}$). Water from Well UE25p#1 taps the carbonate aquifer that underlies the repository horizon (pH of 6.7, moderately reducing Eh). This water has an ionic strength and total carbonate content an order of magnitude higher than those in J-13 water[3]. The apparent solubility measurements will be conducted at 25, 60, and 90°C. The pH values selected for making measurements are 6, 7, and 8.5. This presupposes that only order-of-magnitude changes in the hydrogen ion concentration can be expected from the original value of the Yucca Mountain groundwater. Since the carbonate ion concentration will be maintained at the amount the water had in its original state, carbon dioxide partial pressure and pH will be maintained through out the experiments. The pH-stat is described in detail elsewhere[4]. Some experiments are planned using various ionic strength solutions since some evidence suggests that water in the unsaturated zone may have high concentrations of dissolved species. Also planned are experiments using two different isotopes of the same element (e.g. ^{239}Pu; $t_{1/2}=2.41 \times 10^4$ yr. and ^{242};Pu $t_{1/2}=3.76 \times 10^5$ yr) in order to investigate the effects of different radiation fields. The Eh and concentration and speciation of the radionuclides are measurable parameters dependent on the conditions outlined above. In these apparent solubility experiments, upper and lower limits will be determined in most cases by approaching the solubility from both oversaturation and undersaturation. Therefore, if true thermodynamic equilibrium is not attained, then the solubility range will be bracketed.

Speciation

Speciation is strictly defined as (1) the identity of the radionuclide, (2) determination of its oxidation state, and (3) the formula and/or structure of the ionic and/or soluble complex. Speciation can be determined to a lesser degree by determining only the oxidation state(s) of the radionuclides. Although apparent solubility measurements will provide limits for radionuclide concentrations under specific groundwater conditions, they cannot possibly provide data for all forseeable groundwater conditions. Therefore, a fundamental thermodynamic characterization of radionuclide speciation is required to bridge any gaps in that data acquired from direct solubility measurements and to provide the fundamental thermodynamic constants needed for the solubility modeling task. In this study we will attempt to identify the important complexes of the radionuclides and their complexation quotients. Ogard and Kerrisk[3] report that carbonate ions are the principal potential complexing agents in the Yucca Mountain groundwater for the actinide elements uranium, neptunium, plutonium, and americium. These actinides, which typically have quite low solubilities in near neutral groundwaters, can be strongly complexed by "hard" (ionic)

oxygen–donor ligands to form species that have greatly increased solubility limits. For this reason, the speciation study will focus on the carbonate complexes of actinides, but additional work is planned to study other potentially important complexing ligands commonly found in groundwater (e.g., fluoride, phosphate, humates, etc.).

Carbonate ion speciation of the actinides under relevant repository conditions involves equilibria such as

$$Pu^{4+} + mHCO_3^- + nH_2' \rightleftharpoons [Pu(OH)_n(CO_3)_m]^{4-n-2m} + (n+m)H^+. \qquad (1)$$
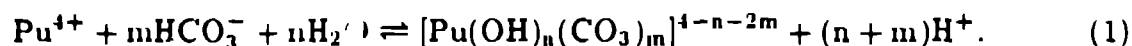
It is difficult to study these equilibria directly using conventional analytical methods because at environmentally relevant pH values, the concentration of Pu^{4+} is extremely low and well below the sensitivity limits of conventional methods. We are currently pursuing two of the most promising approaches to dealing with this problem. The first approach is the method of competitive complexation[5]. This method utilizes conventional electronic absorption spectroscopy to obtain speciation data. This approach requires deviation from site–specific conditions so that sufficiently high radionuclide concentrations (10^{-3} $\underline{M}$ can be maintained and detected by absorption methods. In order to bridge the gap between the well-characterized free ion, such as Pu^{4+} at low pH values, and the highly complexed hydroxycarbonate complex at high pH values, an intermediate competitive complexing ligand is used. We use citrate ion for this study. Previous work shows that carbonate ions successfully compete with citrate ions for the coordination of actinides. Three steps are required in this study; we must investigate (1) the pure carbonate/actinide system; (2) the pure citrate/actinide system, and (3) the mixed carbonate-citrate/actinide system. This will ultimately permit expression of the carbonate formation constants for Equation 1, in terms of the principal radionuclide species present in solution (e.g., Pu^{4+}).

The second approach to speciation studies does not use conventional analytical methods. We are developing ultra sensitive laser–based spectroscopic techniques for direct spectral detection of species under relevant site specific conditions at ambient concentrations ($< 10^{-8}$ $\underline{M}$). These techniques include the absorption based probes photoacoustic spectroscopy (PAS), and the related method of photothermal deflection (PDS), and the complimentary, emission based probe, laser induced fluorescence (LIF) spectroscopy. Ultimately, electronic spectra are obtained by all of the above methods and the goal is to extract structural information. The electronic spectra of actinides are dominated by characteristically narrow f f transitions which are quite sensitive to electronic environmental

changes brought about by the perturbation of the complexed ligand. However, the relationship between spectral signatures and structures must generally be established empirically. Accordingly, part of our task will be to establish these spectral signatures for the various actinide species extant under site–specific groundwater conditions.

Colloids

A subtask of the speciation task is the study of colloid formation, characterization and stability. The potential for radionuclide movement in groundwater is based not only on soluble ionic species, but on colloidal particulates as well. Additionally, these colloids could break up to form ionic species as an additional source of soluble radionuclides.

There are essentially three types of colloids: radiocolloids, natural colloids, and psuedocolloids. Radiocolloids are pure particles of the radionuclides. Natural colloids are particles of natural minerals, which are generally not radioactive. Psuedocolloids are natural colloids which have been "combined" with ionic or solid forms of radionuclides. In the solubility/speciation task, we will concern ourselves only with true radiocolloids.

To assess the potential for radiocolloid transport, information is needed concerning the likelihood of colloid formation under water conditions at the Yucca Mountain site and the stability of colloids once formed. Two radionuclides that may form stable colloids under these conditions have been identified: plutonium and americium. In order to understand the behavior of these colloids in Yucca Mountain groundwater, it is important to study both their physical and chemical properties. The most important physical characteristics are particulate size, density, and bulk charge. These characteristics determine transport/retardation mechanisms such as filtration, adsorption, sedimentation, etc. The most important chemical properties are chemical reactivity and colloid structure. A host of analytical methods are being brought to bear on this study including, absorption, diffuse reflectance, and auto-correlation spectroscopies, centrifugation, filtration, chemical and electrochemical redox methods, and x-ray diffraction and absorption fine structure methods.

Sorption

The sorption studies are designed to obtain values for sorption coefficients for use in performance assessment calculations and to obtain insight into the mechanisms by which various radionuclides sorb onto tuffaceous materials. Such insight will enhance confidence in use of the empirically measured sorption coefficients. Thomas[6] has compiled a database

of sorption ratios obtained by batch techniques for most of the important radionuclides in spent fuel. The ratios in this database are for certain rock types and ground waters found in the Yucca Mountain site. Many of the coefficients in the database, particularly those for the actinides are not sufficiently reliable to be used in performance assessment calculations in support of a license application. The following discussion outlines the present uncertainties in the database and outlines our approach regarding their resolution.

Experimental Artifacts

Batch sorption experiments are conceptually simple and basically involve contacting a given volume of ground water from the site, spiked with the radionuclides(s) of interest, with a portion of crushed solid material either from the site or representative of some mineral species present within the site. After some predetermined contact time, the concentrations or radioactivities of the elements of interest are measured in the solution and solid and a sorption ratio is calculated[7].

Experimental artifacts that can complicate the interpretation of the data obtained include dissolution of the substrate (i.e. crushed rock) during the experiment and precipitation. Dissolution of the substrate influence the measured sorption ratios primarily through the formation of colloidal and other fine particulates (i.e. disaggregation). The formation of colloids or fine particulates is problematic if they cannot be efficiently separated from the solution prior to the concentration analysis[8]. For radionuclides with high sorption coefficients, small amounts of colloid or particulate material remaining in the solution will not only result in underestimation of the sorption coefficient but will complicate the interpretation of the experimental data in terms of possible sorption mechanisms. We have found that ultrafiltration (i.e. 0.03 micron pore size) appears to remove most of the colloidal material from solution. Ultracentrifugation appears to be a less efficient technique for the solid-liquid separations.

Precipitation can also have an appreciable effect on the measured sorption ratios particularly for elements such as the rare earths, americium and plutonium. The solubilities of compounds of the actinides americium and plutonium in Yucca Mountain ground waters have only recently been quantified to an acceptable level[9]. The new results indicate these solubilities are significantly smaller than previously thought. Because the sorption ratios for americium and plutonium reported in Thomas[6] were obtained with solution having higher concentrations than the measured solubilities, these ratios are called into question. We have initiated a new set of experiments using solutions that have concentrations below

the current estimates of solubilities for these elements. This poses an analytical problem in that the solution concentrations of these elements in a typical sorption experiment tend to be very low because these elements have rather large sorption coefficients. To analyze these concentrations we have developed mass spectrometric isotope dilution procedures which allow accurate determination of americium and plutonium down to the picogram level.

Batch laboratory experiments vs. field setting

Because the hydrologic regime in Yucca Mountain is complex sorption ratios measured in the laboratory on crushed rock material must be used with caution. Factors that could effect the applicability of these ratios include (1) fracture vs. matrix flow, (2) variability of substrate composition, (3) variability of ground water composition, (4) changes in water/rock ratios, (5) the number of sorption sites accessible to the flowing groundwater in crushed vs. in situ rock, (6) colloid transport, (7) sorption reaction kinetics, and (8) complex source term (i.e. waste package) solutions. Although resolution of these issues will involve the results of various types of investigations, appropriate sorption experiments are a prerequisite.

The first two problems can be addressed largely through batch experiments on samples of pure minerals found along fractures and within the matrix of rock units in Yucca Mountain. Factor number three can be bounded by experiments involving the end-member water compositions presently found within Yucca Mountain or anticipated in the future and pure minerals or whole-rocks. Changes in water/rock ratios can be addressed with isotherm measurements on appropriate rock and mineral samples[7]. Data on the number of sorption sites available in in situ rock vs. crushed rock can only be obtained by carrying out laboratory and field experiments involving solid rock. Because these experiments are difficult to carry out and interpret, their number will be much more limited and they must be designed to provide the maximum probability for success. Batch sorption experiments can be used to further these goals. Colloidal transport complicates the application of sorption ratios in transport calculations because colloids offer an independent mode of transport that is not addressed in the typical sorption experiment. However, batch sorption experiments can measure the degree to which important radionuclides are sorbed on the colloids once the colloids are identified in sufficient detail. Sorption kinetics can be studied directly by batch experiments carried out in a time series[10]. The results of such studies can be compared with the results of column experiments in which the flow rate is a variable.

Sorption Mechanisms

Understanding of the mechanisms or reactions by which radionuclides sorb to geologic materials will aid in the validation of empirically determined sorption ratios and improve confidence in the application of the ratios. Possible sorption mechanisms appropriate to the Yucca Mountain site include (1) ion exchange on minerals such as clays and zeolites, (2) surface complexation reactions on iron and manganese oxides and oxyhydroxides, framework silicates such as quartz and feldspar, and possible phosphates and carbonates, and (3) precipitation in solid solutions of carbonates, phosphates, or other low temperature minerals. Ion exchange reactions in minerals such as clays and zeolites are well documented and theoretically understood[11]. For these reactions, the sorption ratios determined on crushed samples are not very different from ratios determined on solid samples[12] because the exchange sites are largely intracrystalline. Therefore, the value of the sorption coefficient for simple cations in given rock is largely a function of the zeolite and clay content of the rock[7].

The behavior of the actinides americium, plutonium and neptunium appear more complicated as no simple correlations between sorption ratios and the abundances of the major ion exchange minerals have been observed[7]. These elements, in complexed form, may sorb dominantly by surface complexation reactions. Iron and manganese oxide and oxyhydroxide minerals appear to have a strong affinity for these elements presumably as a result of such reactions[13]. Because americium and plutonium have rather low solubilities in dilute ground water solutions, studies of sorption mechanisms for these elements are difficult to carry out without using oversaturated solutions. However, the higher solubility of neptunium compounds have allowed the use of spectroscopic techniques such as EXAFS and XANES in the investigations of sorption mechanisms.

The mechanisms by which anionic species sorb is also of great interest because some important radionuclides such as technetium are dominantly in anionic form in environments representative of the Yucca Mountain site. Although the sorption of these species is likely minimal, it is important to measure the ratios as accurately as possible. In this regard, the know affinities of iron and manganese oxide and oxyhydroxide minerals will be investigated in some detail.

Radionuclide Transport

The theory of transport through porous media were developed primarily for chemical engineering[14]. The theoretical methods were developed with the principal purpose of

designing efficient separations processes for the chemical industry using chromatographic columns. Chromatographic columns are generally homogeneous with respect to both hydraulic properties, i.e., porosity and permeability, and chemical properties. Transport in geologic media is on the other hand complex hydrologically and chemically. Hydrologists have successfully applied the principles developed for column chromatography using the simplifying assumption of a representative elementary volume, REV[15]. However, the assumption of an REV is only valid under special circumstances. A general approach to modeling transport in complex hydrologic systems has yet to be developed.

The problem is to develop an approach which minimizes the level of detail required to make predictions within a required level of certainty. Modern stochastic models[16,17,18] capable of calculating the transport of conservative tracers describe the heterogeneity of aquifers in terms of the covariance of the permeability distribution. Spatial covariance is a property observed in Fractal geometry[19] and other nonlinear phenomena, such as, cellular automata. This opens many avenues for generating realistic models of hydrologic transport. The effect of the spatial variation of the geochemical and/or sorptive properties with respect to transport has not been calculated. A concern in terms of making accurate predictions of radionuclide migration is the effect of covariance between permeability and sorption. For example, if the highly sorptive minerals, such as, smectites, correlated with zones of low permeability. Then the radionuclides contained in the fastest water would in addition have a retardation factor below average. This could greatly increase the observed dispersion and lead to early breakthrough of small quantities of radioactive waste.

The Dynamic Transport task has as its primary mission the task of testing the assumptions made in the theory of chromatography and hydrologic transport by experimentally observing the transport of radionuclides in laboratory to field scale experiments, and a secondary mission of validating the sorption results in tuff columns of varying complexity. The simplest experiments are performed with crushed tuff uniformly packed in acrylic columns. These experiments utilize crushed tuff prepared in the same manner as the crushed tuff used by the sorption task. Significant discrepancies could indicate the presence of coexisting chemical species of the same element, colloid formation, and/or pseudocolloid formation. The kinetics of sorption can be studied by varying the water velocity and measuring the dispersion of the breakthrough curve as a function of velocity.

The results of crushed tuff columns have yielded the following conclusions. The observed retardation factors for alkali metals and alkaline earths have agreed with those

predicted from batch sorption measurements of K_d using the equation[20,21],

$$R_f = 1 + \frac{K_d \rho}{\epsilon}.$$

The actinides neptunium and americium on the other hand have exhibited unretarded breakthrough[22]. For americium the amount which elutes early is a small fraction usually ~ 1 percent of the total americium injected.

The next level of complexity is to perform radionuclide migration experiment with intact tuff columns. These columns will not have the hydrologic simplicity that the uniform packing of sieved crushed tuff provides. They will however be free from the uncertainty that crushing causes in terms of the surface properties of minerals. These samples retain the natural hydrodynamic dispersion (valid for the laboratory scale) for porous flow through the tuff matrix. These experiments have produced interesting results. Samples of densely welded tuff from the Topopah Spring member, Yucca Mountain, Nevada have exhibited elution curves which cannot be fit to the conventional advection-dispersion equation, ADE[23]. The curves can be fit however with a time dependent equivalent dispersion coefficient[24]. This phenomenon was theoretically shown to be the result of the spatial distribution of permeability by Matheron and de Marsily[16]. Themost dramatic consequence of the time dependent dispersion is the effect on the prediction of breakthrough times for sorbing tracers. If the conventional ADE is employed to predict the breakthrough of strontium the expected breakthrough in the solid tuff column would be at ~ 1.5 years, based on batch sorption measurements. The actual breakthrough occurs within a few weeks of the start of the experiment. This is a discrepancy of greater than an order of magnitude. If the dispersion is given a time dependence the elution curve can be fit with the measured batch sorption coefficient. The observation of time dependent dispersion in laboratory scale migration experiments has provided new insight into the effect of heterogeneity on the retardation of sorbing radionuclides. Time dependent dispersion has been observed in the tritium elution from the CAMBRIC field test in tuffaceous alluvium on the Nevada Test Site for the Hydrology Radionuclide Migration Project[25]. The question which arises from these column experiments is when can one expect to observe the elution of sorbing radionuclides from CAMBRIC.

The next level of complexity is achieved with fractured tuff. In fractured rock the fluid flows through discrete fractures with a characteristic dispersion dominated by the variation in permeability within the fracture. Tracers will diffuse into the rock matrix perpendicular

to the fracture as first pointed out by Neretnieks[26]. Radionuclide migration experiments in saturated tuff fractures have confirmed the importance of matrix diffusion. Elutions of conservative tracers can be described adequately by the analytic solution to the advection dispersion equations of Tang et al[27]. Adjustment of the fracture aperture from the cubic law aperture determined from the fracture permeability is required to fit tracer data in some fractures. Elutions with sorbing tracers have exhibited some early breakthrough due to pseudocolloid formation or channeling. It may be possible to model the latter with time dependent dispersion in the fracture. Colloidal tracers have exhibited a peculiar shift in apparent fracture aperture with colloid diameter. This phenomenon has not been fully explained but is possibly the result of channeling. More transport experiments with tuff fractures and more detailed characterization of the water flow paths through the fracture are required to advance the understanding of radionuclide migration in discrete fractures.

Conclusions

In summary, we are performing research on chemical and physical processes important to conducting a performance assessment of the Yucca Mountain Site, Nevada. The information generated will increase the confidence and decrease the uncertainty in the long-term predictions of radionuclide migration. The specific research being conducted includes:

1. Experimental determination of solubility limits of fission products and actinides including the collection of thermodynamics data.

2. Experimental determination of chemical speciation of important fission products and actinides through the use of new spectroscopic methods.

3. Experimental determination of the size, structure and chemical behavior of radio-colloids.

4. Basic understanding of factors leading to uncertainty in the sorption database and development of new experimental techniques and methods to reduce these uncertainties.

5 Analytical and experimental program to understand basic sorption mechanisms (e. g. EXAFS).

6 Basic understanding of factors leading to uncertainty in the transport mechanisms of advection, diffusion, and dispersion through the use of experiments and theory development.

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